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LETTER

Regioselective synthesis of pyrimidine-annulated spiro-dihydrofurans by silver-catalyzed 5-*endo-dig* cyclization†

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A simple and efficient method for the synthesis of some hitherto unreported pyrimidine-annulated spiro-dihydrofurans has been described. In the presence of $AgSbF_6$ spiro- and furo-pyrimidine (10-hydroxy-4,7,9-substituted-1-oxa-7,9-diazaspiro[4.5]dec-3-ene-6,8-dione) heterocycles are obtained in good yields. The nature of the alkyne moiety present in substrates dictates the mode of cyclization to form the furopyrimidine derivatives.

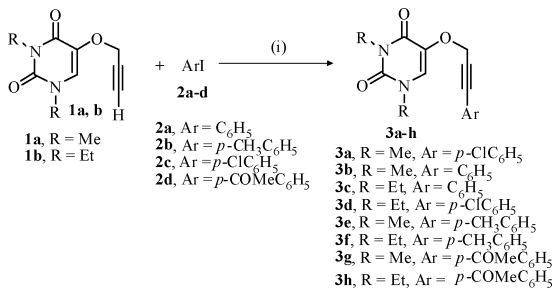
Pyrimidine, being a component of nucleic acids, exhibits diverse role in biological, pharmaceutical as well as agrochemical sectors. A number of pyrimidine-based molecules like BVDU (*E*)-5-(2-bromovinyl)-2′-deoxyuridine, Zidovudine, Stavudine are well known as therapeutic agents due to their anti-cancer and anti HIV properties.[1] It is well established that furo[2,3-*d*]-pyrimidine[2] and spiropyrimidine[3] derivatives have desirable pharmacological properties. Among them, the furo[2,3-*d*]-pyrimidine derivatives act as sedatives, antiulcer agents, muscle relaxants, antihistamines and diuretics.[4] Moreover some of the furopyrimidine derivatives are potent and selective anti-VZV agents.[5] Introduction of a functionality at the C-5 and C-6 positions of uracil leads to biologically interesting molecules. Synthesis of furan fused pyrimidines is important because of their broad spectrum of biological activities. Comparatively little efforts have been made for the synthesis of furopyrimidine derivatives[6] and spiro-pyrimidine derivatives.[7] Reported methods involve either multisteps[7a] or require harsh reaction conditions.[7d] Due to these limitations we have planned to develop a simple and short protocol for the synthesis of furopyrimidines.

In continuation of our work on the pyrimidine-annulated heterocycles,[8] we have recently reported[9] a novel method for the synthesis of pyridopyrimidine derivatives by $AgSbF_6$ catalyzed reaction of 5-(*N*-propargyl)pyrimidines *via* a 6-*endo-dig* mode of cycloisomerization. To our knowledge, there is no report on the synthesis of bioactive furo-pyrimidine derivatives by silver-catalyzed reaction. As shown in recent literature data[10] silver-catalyzed reactions have received less attention. This has prompted us to study the reaction of propargyloxypyrimidine substrates with $AgSbF_6$. Herein we report the results of our investigation.

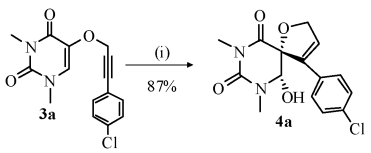
The required precursors **3a–h** for this study were prepared in excellent yields by the Sonogashira cross coupling reaction of the substrates **1a, b** (1 equiv.), aryl iodides (1.2 equiv.) using $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%) as co-catalysts in anhydrous DMF and Et_3N (10 : 3) at room temperature (Scheme 1).

After a series of trials, we observed that 5-propargyloxy-pyrimidine **3a** could undergo a reaction with $AgSbF_6$ (0.1 equiv.) in HOAc at 80 °C to afford selectively a new compound in 87% yield (mp 172 °C) (Scheme 2).

The spectral and analytical data of the compound showed the formation of the product **4a**. IR spectroscopy indicated the presence of a hydroxyl group at 3345 cm^{-1} which was confirmed by D_2O-exchange NMR spectroscopy. Finally, the structure of the spiro heterocyclic product **4a** was established from the single crystal X-ray diffraction analysis[11a] (Fig. 1). Refinement has been carried out including the hydrogen atom at calculated positions except H8, H8A, H8B and H9. These hydrogens have been located and refined isotropically. From the X-ray analysis it is clear that compound **4a** is



Scheme 1 *Reagents and conditions*: (i) $Pd(PPh_3)_2Cl_2$, CuI, anhyd. DMF and Et_3N, rt, 1 h.



Scheme 2 *Reagent and conditions*: (i) $AgSbF_6$, HOAc at 80 °C, 4 h.

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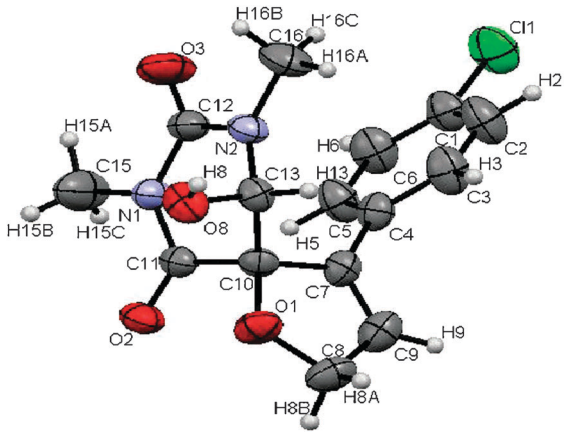


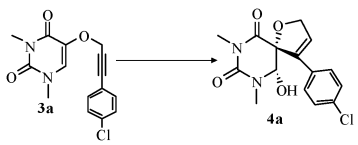
Fig. 1 The ORTEP diagram of the compound **4a**.

cis-substituted with respect to the ring substituents *i.e.* hydroxy (–OH) group and ether (–O–) linkage.[11b]

However, to optimize the reaction conditions, in order to obtain a maximum yield of the cyclized product, a set of experiments were carried out with the substrate **3a** by changing the parameters (solvent, catalyst), see Table 1.

When the reaction was run in the presence of $AgSbF_6$ in HOAc, an excellent yield of the compound **4a** (87%, entry 1) was obtained. Among the different catalysts used $ZnCl_2$ and $AlCl_3$ (entries 9 and 12) gave very poor yield of the products (19–21%), but Cu(I) and Cu(II) gave somewhat better results (27–40%, entries 6–8). We have obtained a moderate yield of **4a** when the reaction was carried out with $AuCl_3$ (48%, entry 19). But when $AuCl_3$ was used along with $AgSbF_6$ the yield of the product **4a** increased to 82% (entry 20). However, when the reaction was carried out with $AgBF_4$ a good yield (68%, entry 21) of the product was obtained. Other silver catalysts like $AgNO_3$, AgOTf, AgOAc and AgI also gave the same product but in moderate yields (28–52%, entries 5 and 22–24,). Polar aprotic solvents like DMSO and acetonitrile, failed to give any cyclized product. The reaction was also unsuccessful in toluene (entry 4).

Table 1 Optimization of spiro cyclization of compound **3a**



Entry	Catalyst[a]	Solvent	Temp./°C	Time/h	Yield[b] (%)
1	**$AgSbF_6$**	**HOAc**	**80**	**4**	**87**
2	$AgSbF_6$	DMSO	80	15	—
3	$AgSbF_6$	CH_3CN	Reflux	15	—
4	$AgSbF_6$	Toluene	Reflux	15	—
5	$AgNO_3$	HOAc	80	4	44
6	CuI	HOAc	80	4	34
7	$Cu(OAc)_2$	HOAc	80	4	40
8	$CuSO_4{\cdot}5H_2O$	HOAc	80	4	27
9	$ZnCl_2$	HOAc	80	4	19
10	$NiCl_2{\cdot}2H_2O$	HOAc	80	4	cm
11	$FeCl_3$	HOAc	80	4	cm
12	$AlCl_3$	HOAc	80	4	21
13	—	HCl	80	9	—
14	—	H_2SO_4	80	9	—
15	—	TfOH	80	9	—
16	—	HOAc	80	9	16
17	—	H_2O	Reflux	17	—
18	—	DMSO, H_2O[c]	80	15	—
19	$AuCl_3$	HOAc	80	6	48
20	$AuCl_3$, $AgSbF_6$[d]	HOAc	80	4	82
21	$AgBF_4$	HOAc	80	4	68
22	AgOTf	HOAc	80	4	46
23	AgOAc	HOAc	80	4	52
24	AgI	HOAc	80	4	28

[a] Reactions (entries 1–12) were carried out with 1 equiv. **3a** and 0.1 equiv. of catalyst. Reactions (entries 13–6) were carried out in the presence of Bronsted acids. [b] Isolated yield. [c] Both solvents were used in the same ratio cm = complicated reaction mixture. [d] Both catalysts were used in the same ratio.

However it is remarkable that only HOAc, among various solvents used, gave the fruitful result. When the reaction was carried out in HOAc without any catalyst we obtained the cyclized product within 9 h in very poor yield (16%, entry 16). According to Toste *et al.*, the coinage metal catalysts accelerate the cyclization reaction by producing related Brønsted acids in the reaction medium.[12] We have also carried out the reaction in the presence of Brønsted acids like HCl, H_2SO_4, triflic acid but did not get any product (entries 13–15). Thus here, HOAc might have a role in facilitating the reaction with a silver catalyst. Other Lewis acids $FeCl_3$ and $NiCl_2{\cdot}2H_2O$ resulted in the formation of a complicated reaction mixture (entries 10 and 11). The reaction was also carried out in H_2O and DMSO–H_2O mixture (entries 17 and 18, Table 1) but we did not get any product. After a series of experiments was performed, the optimized condition developed so far was treatment of the substrate with 10 mol% $AgSbF_6$ in HOAc at 80 °C (entry 1,Table 1).

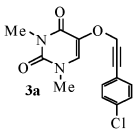
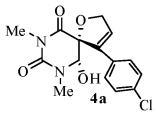
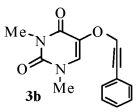
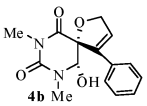
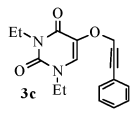
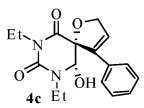
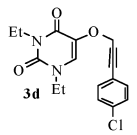
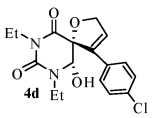
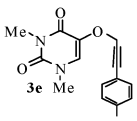
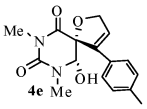
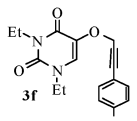
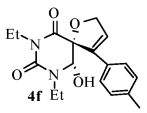
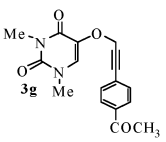
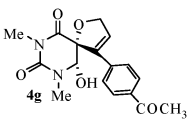
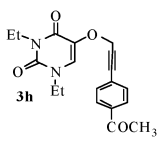
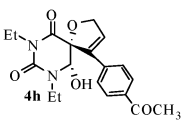
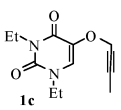
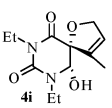
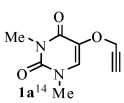
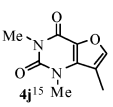
This optimized reaction condition was used for the other substrates. Treatment of **3b** under the optimized condition afforded the product **4b** in 78% yield. Similarly the compounds **4c**, **4d**, **4e** and **4f** were obtained from their corresponding starting materials **3c**, **3d**, **3e** and **3f** in 75%, 84%, 80% and 82% yields respectively. The products **4g** and **4h** were obtained from **3g** and **3h** in 5 h with 69% and 62% yields respectively. When the substrate **1c** was subjected to the optimized condition for 4.5 h the corresponding spiro-dihydrofuran **4i** was obtained in 59% yield. All the spiro-dihydrofurans are *cis* with respect to ether linkage and hydroxy group. The results are summarised in Table 2.

When 1,3-dimethyl-5-propargyloxyuracil **1a** was treated under the optimized condition (*i.e.* 10 mol% $AgSbF_6$ and HOAc) 1,3,7-trimethylfuro[3,2-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (**4j**) was obtained in 85% yield instead of the spiro-dihydrofuran (Table 2, entry 10).

Kawahara *et al.* have reported[13] the formation of the keto product **5a** from 1,3-dimethyl-5-propargyloxyuracil (**1a**) in the presence of acid (Scheme 3). However, neither HOAc nor H_2SO_4 gave the corresponding keto product from the substrate **3a**. Therefore the Ag(I) catalyst may be responsible for this type of cyclization.

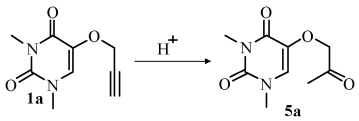
From the results shown in Table 2, it is observed that in the case of the nonterminal alkynes the reaction shows high regioselectivity to give only the spiro-heterocycles. The reaction proceeds *via* a 5-*endo-dig* mode of cyclization (through path a, Scheme 4). But in the case of a terminal alkyne the reaction

Table 2 $AgSbF_6$ catalyzed synthesis of furopyrimidine derivatives

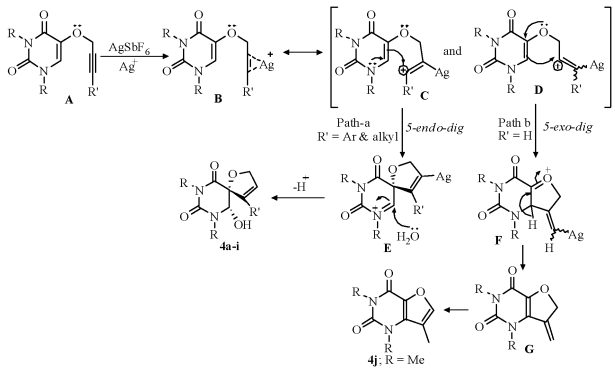
Entry	Starting materials (**3**)	Time/h	Products (**4**)	Yield[a] (%)
1	 **3a**	4	 **4a**	87
2	 **3b**	4.5	 **4b**	78
3	 **3c**	4.5	 **4c**	75
4	 **3d**	4.5	 **4d**	84
5	 **3e**	4.5	 **4e**	80
6	 **3f**	4.5	 **4f**	82
7	 **3g**	5	 **4g**	69
8	 **3h**	5	 **4h**	62
9	 **1c**	4.5	 **4i**	59
10	 **1a**[14]	4.5	 **4j**[15]	85

[a] Isolated yield.

proceeds *via* a 5-*exo-dig* mode of cyclization (path b, Scheme 4). According to Baldwin's rule[14] both the modes (5-*endo-dig* and 5-*exo-dig*) are favourable for the formation of a 5-membered ring. The results show that the mode of cyclization was controlled by the nature of the alkyne moiety of the enyne part of the substrates. On the basis of the above results, the formation of the products may be rationalized. Initially a π-complex **B** may be formed between an alkyne segment of the substrate **A** and a silver ion (Scheme 4). The formation of products can be explained *via* the formation of



Scheme 3



Scheme 4 Plausible mechanism for the synthesis of furopyrimidines.

carbocations (**C** and **D**) from the π-complex **B**. When R′ = H, carbocation **D** is more stable compared to **C**, but when R′ = Me or Aryl, carbocation **C** is stabilized by the +M effect of the phenyl ring or the +I effect of the –Me group present in the terminal part of the alkynes.

The spiro-dihydrofurans may also be assumed to form by a 5-*endo-dig* mode of cyclization of **B** *via* formation of carbocation **C**. The involvement of a lone pair of the N atom of the pyrimidine ring may facilitate this mode of cyclization by formation of a Mannich species[10e,f] **E**. Then H_2O may attack the imino bond from the opposite side of the substituent –R′ to avoid the steric crowding to afford the spiro-dihydrofurans **4a–i** (path a). Thus stereoselectivity of the reaction is controlled by a steric factor. The formation of the furo-fused pyrimidine **4j** can be explained by a 5-*exo-dig* mode of cyclization of **B** *via* **D** to **F** followed by isomerization of **G** (to gain aromaticity). The yields of regioselective formation of the spiro-dihydrofurans may also be rationalized by the nature of the group present on the alkyne terminal; a more electron donating group which stabilized the carbocation **C** gave the better yield compared to the electron withdrawing substituent (–$COCH_3$).

Herein we have developed a new straightforward methodology for the regioselective as well as stereoselective synthesis of hitherto unreported pyrimidine annulated spiro-heterocycles from propargyloxyuracil by the $AgSbF_6$ catalyst in HOAc medium *via* a 5-*endo-dig* mode of cyclization, which was totally controlled by the nature of the acetylenic moiety of the ether substrate. Sames *et al.* have reported[15] cyclization of propargyl ether with different catalysts but failed to obtain any furano derivative. Generally $AgSbF_6$ is used to activate the gold-catalyst.[10a,16] But this is an example of silver mediated hetero-1,5-enyne cyclization which is currently a topic of general interest. The observed 5-*endo* cyclization mode is rare[17] for such reactions where, the 6-*endo* mode seems to be more common.[18] To our knowledge this is the first report for this type of spiro heterocyclization solely by the silver catalyst.

In conclusion, we have developed a novel and efficient method for the regioselective and stereoselective synthesis of hitherto

unreported 4,7,9-substituted-10-hydroxy-1-oxa-7,9-diazaspiro[4.5]-dec-3-ene-6,8-dione derivatives from various *O*-propargylated uracil derivatives by a silver-catalyzed 5-*endo-dig* mode of cyclization which is controlled by the nature of the substituents at the terminal alkyne moiety of the substrates.

General procedure for the preparation of compound 3a–h and 1c

A mixture of the compounds **1a** (500 mg, 2.74 mmol), *p*-chloroiodobenzene (786 mg, 3.29 mmol), $Pd(PPh_3)_2Cl_2$ (0.13 mmol) and CuI (0.27 mmol) in dry DMF (5 mL) and dry Et_3N (1.5 mL) was stirred at room temperature for 1 h. After completion of the reaction (as monitored by TLC), the reaction mixture was poured in water. This was extracted with dichloromethane (3 × 15 mL). The combined organic extract was washed with brine (1 × 15 mL) and dried over Na_2SO_4. The solvent was distilled off. The resulting crude product was purified by column chromatography over silica gel (60–120 mesh) using a petroleum ether–ethyl acetate mixture (4 : 1) as an eluent to give the product **3a**. Similarly precursors **3b–h** were prepared from the corresponding iodobenzene derivatives. The compound **1c** was prepared by refluxing 1,3-diethyl-5-hydroxypyrimidine-2,4(1*H*,3*H*)-dione (1 g, 5.4 mmol) with 1-bromobut-2-yne (0.85 g, 6.4 mmol) and anhydrous K_2CO_3 (1.5 g, 10.8 mmol) in acetone (75 mL) for 5 h and purified by column chromatography using a petroleum ether–ethyl acetate mixture (3 : 2) as an eluent.

General procedure for the preparation of compounds 4a–j

To a stirred solution of $AgSbF_6$ (9 mg, 0.026 mmol) in HOAc (5 mL), 5-(3-(4-chlorophenyl) prop-2-ynyloxy)-1,3-dimethyl-pyrimidine-2,4(1*H*, 3*H*)-dione **3a** (100 mg, 0.26 mmol) was added at room temperature and stirred at 80 °C for 4 h. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled and neutralized with saturated $NaHCO_3$ solution. This was extracted with dichloromethane (3 × 10 mL). The combined organic extract was washed with brine (1 × 10 mL) and dried over Na_2SO_4. The solvent was distilled off. The resulting crude product was purified by column chromatography over silica gel (60–120 mesh) using a petroleum ether–ethyl acetate mixture (2 : 3) as an eluent to give the product **4a**. Similarly compounds **4b–j** were obtained from the corresponding precursors.

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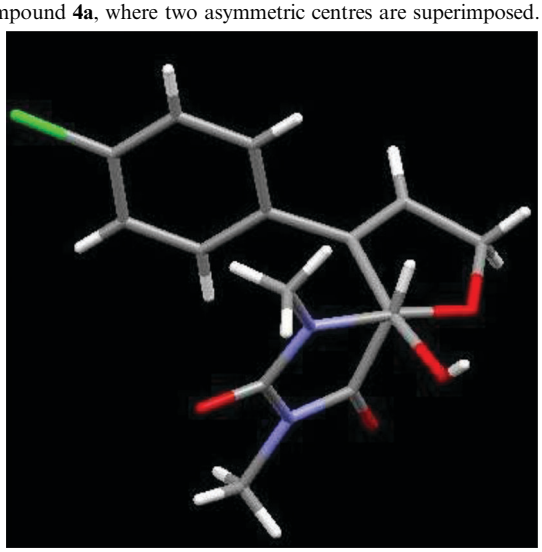

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